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2 Pic (d) Direct O₂

Electron-stimulated O⁻ desorption from O₂ condensed on a rare-gas film: Evidence for an indirect "bounce" trajectory.

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2 Pic (d) Direct O₂

1. INTRODUCTION

The electron-stimulated O⁻ dissociation or O₂ gas is well understood [1]. In the energy range from 4 to 10 eV, O⁻ ions are produced by dissociative attachment (DA) via the transient O₂(¹D₁) state. This same DA process has been identified in electron-stimulated desorption (ESD) of O⁻ ions from O₂ condensed on thick rare-gas (Ar, Kr, or Xe) films [2]. However, electron-energy-dependence curve of the O⁻ yield is quite different from that for gaseous O₂, shown in Fig. 1. The gas-phase curve rises slowly at the threshold and has a symmetric bell shape, while the condensed-phase curve rises sharply at the threshold and has an asymmetric triangular shape. Furthermore, the threshold energy of the condensed-phase curve depends on the rare-gas substrate, as shown in Table 1. In this note, we offer an explanation for the threshold changes and suggest a trajectory for the O⁻ ion desorption via the O₂(¹D₁) intermediate state. We shall explain the different energy dependence elsewhere [3]. (R.W.)

2. DISCUSSION

2.1 Two possible trajectories

Figure 2 illustrates two possible O⁻ desorption trajectories for an inclined O₂ on a rare-gas substrate. In one trajectory DA yields an O⁻ ion moving away from the surface (we shall call this the direct-path (DP) trajectory), while in the other it yields an O⁻ ion moving initially towards the surface requiring it to "bounce" off the surface (we shall call this the indirect-bounce (IB) trajectory). The schematic potential curves which lead to these two trajectories are illustrated in Fig. 3. In the IB case, the O₂(¹D₁) intermediate state dissociates into the O+O/RG limit, which means that the O⁻ ion initially ends on the rare-gas (RG) surface, while in the DP case, it dissociates into the O+O/RG limit, which indicates that the O⁻ ion proceeds directly from the surface. The O+O-polarization energy (E_p) of the RG limit by the surface-Condon region, the potential curves for the DP and IB trajectories become the same and are lowered by E_p, with respect to the gas-phase potential curve as shown in Fig. 1.

Fig. 1. Comparison of the ESD O⁻ yields from (a) gaseous O₂ and (b) O₂(0.03 ML)/Kr(20 ML)/Pt.

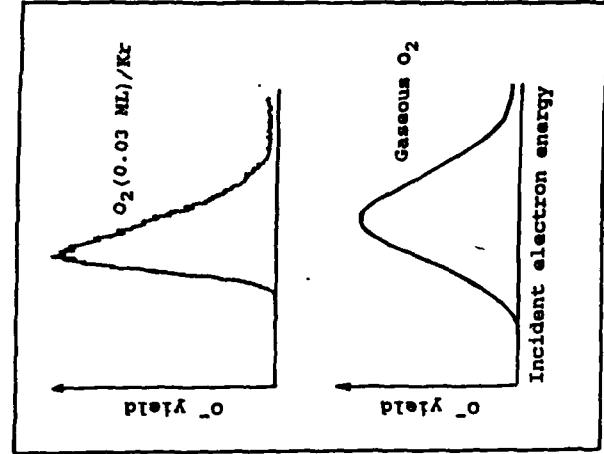


Table 1. Threshold energies (eV) for the O⁻ yield from O₂/RG.

RG -	Ar	Kr	Xe
Experiment	4.3	4.3	4.5
IB trajectory	4.3	4.4	4.5
DP trajectory	3.7	3.7	3.7

2.2 Threshold energy

The threshold energies for O⁻ desorption via the DP and IB trajectories are given by E_d and E_d' respectively, where E_d (=3.65 eV) is the dissociation energy (i.e., difference between O₂ and O+O). The threshold energy (E_{Th}) for the IB trajectory is derived from the equation,

$$E_p = [E_{Th} - (E_d - E_p)]/2,$$

which means that the O⁻ ion created on the surface must have its kinetic energy larger than the surface-polarization energy E_p to desorb from the surface. Threshold energies calculated with the E_d's obtained by Sanche et al. [5] (i.e., 0.62, 0.72, and 0.89 eV for Ar, Kr, and Xe, respectively) are listed in Table 1. The good agreement between the IB threshold energies

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These intuitive potential curves, one might infer that O_2^- ($^2\Pi_u$)/RG dissociates equally into the $O+O/RG$ and O^-+O/RG limits and predict that the branching ratios for the DP and IB trajectories should be about equal for high electron energies. Based on theoretical rules, we shall show below that the O_2^- ($^2\Pi_u$)/RG state dissociates only into the $O+O/RG$ limit, predicting the predominance of the IB trajectory.

The lowest dissociation limit for O_2^- is $O(^3P) + O^-(^2P)$. According to the Wigner-Witmer rules, two O_2^- ($^2\Pi_u$) states and two O^- ($^2\Pi_u$) states arise from the interaction 2^3P the $O(^3P)$ and $O^-(^2P)$ atomic states. The equal number of the O_2^- ($^2\Pi_u$) and O^- ($^2\Pi_u$) states is a consequence of the degeneracy of the $O(^3P) + O^-(^2P)$ and $O^-(^2P) + O(^3P)$ limits. When O_2 is placed on a rare-gas substrate, the two O atoms are no longer identical, e.g., O_p and O_N [farther (F) and nearer (N) from surface]. According to Wigner-Witmer rules, two O_2^- ($^2\Pi_u$) states arise from the $O_p(^3P) + O_N(^3P)$ atomic states and the other two O_2^- ($^2\Pi_u$) states, from the $O_p(^3P) + O_N(^1P)$ limit. According to the non-crossing rule, the lowest two O_2^- ($^2\Pi_u$) states connect to the $O_p(^3P) + O_N(^1P)$ limit, which is the lowest limit since O_N is closer to the surface. The two lowest $^2\Pi_u$ states are the O_2^- ground state and the O_2^- ($^2\Pi_g$) state. Therefore, the O_2^- ($^2\Pi_u$)/RG state connects to the $O+O/RG$ limit. In other words, the O_2^- ($^2\Pi_u$)/RG state dissociates exclusively into the $O+O/RG$ limit.

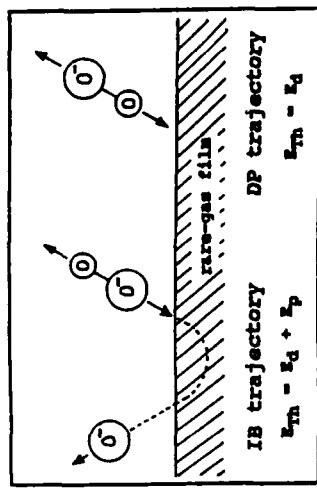
2.4 Cl^- desorption from condensed Cl_2

Cl^- desorption from Cl_2 condensed on Pt provides a clear test of the above arguments.² For this case, only four Cl_2^- states, namely, the $2^3\Pi_u$, $2^1\Pi_u$, and $2^3\Sigma_g^-$ states, arise from the lowest dissociation limit, $Cl^-(^1S) - Cl(^1P)$. Analysis similar to that given above predicts that Cl^- desorption via the Cl_2^- ($^2\Pi_g$) and Cl_2^- ($^2\Pi_u$) intermediate states should follow the IB and DP trajectories, respectively.

The Cl^- ions in the IB trajectory must bounce off the Pt metal for $Cl_2(1\text{ ML})/\text{Pt}$ or off the $Cl_2(4\text{ ML})/\text{Pt}$, where ML=monolayer. Colliding with the Pt metal, the Cl^- ions are most likely neutralized; colliding with the Cl_2 film, the Cl^- ions lose most of its kinetic energy so that it cannot overcome the polarization barrier. [The polarization potential ($\sim 1.5\text{ eV}$) on the Pt metal substrate or the polarization potential ($\sim 1\text{ eV}$) for the thicker Cl_2 film.] Therefore, we expect that Cl^- desorption via the Cl_2^- ($^2\Pi_g$) state, which must follow the IB trajectory, is quenched for both $Cl_2(1\text{ ML})/\text{Pt}$ and $Cl_2(4\text{ ML})/\text{Pt}$.

The ratio of the Cl^- yield peaks via the Cl_2^- ($^2\Pi_g$) and Cl_2^- ($^2\Pi_u$) states is about 1/2 for gaseous Cl_2 [6]. For $Cl_2(1\text{ ML})/\text{Pt}$ and $Cl_2(4\text{ ML})/\text{Pt}$, this ratio nearly vanishes [7] showing that Cl^- desorption via the Cl_2^- ($^2\Pi_g$) state is indeed quenched. This quenching cannot be attributed to angular discrimination, since the Cl^- ions were collected around 70° in the experiment [7] and the $^2\Pi_g$ peak should disappear only if we collect the Cl^-

Fig. 2 Schematic illustrations of the direct-path (DP) and indirect-bounce (IB) O^- desorption trajectories for an inclined O_2 on a rare-gas substrate.



(as opposed to the DP threshold energies) and the observed threshold energies suggests that the O^- desorption via the O_2^- ($^2\Pi_u$) intermediate state proceeds exclusively along the IB trajectory. We note that the DA mechanism involving the IB trajectory is distinctly different from the Antoniewicz "bounce" mechanism [4].

2.3 Potential curve of O_2^- ($^2\Pi_u$)/RG

How does the predominance of the IB trajectory follow from the intuitive O_2^- ($^2\Pi_u$)/RG potential curves in Fig. 3? Based on

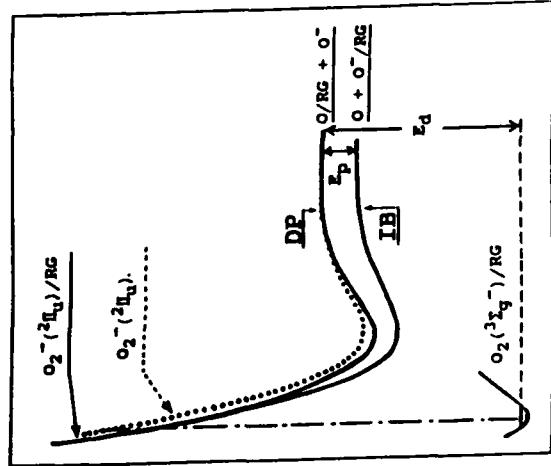


Fig. 3 Schematic O_2^- ($^2\Pi_u$)/RG potential curves corresponding to the DP and IB trajectories. Only the IB curve is valid.

ions exclusively at 90° with respect to the incident electron beam [8]. This quenching also cannot be a discrimination due to a high threshold energy, since the expected peak position (≈ 2 eV) of the $\text{Cl}_2^-(\text{X}^{\prime\prime}\text{Q})$ state is well above the expected threshold energy (≈ 0.0 eV).

The Cl_2^- desorption through the DP trajectory is expected to be similar to that from gaseous Cl_2 : that is, the Cl_2^- ion kinetic energy as a function of the incident electron energy is expected to be a straight line with a slope of $1/2$. This has been observed experimentally [7] for the Cl_2^- ions from the $\text{Cl}_2^-(\text{X}^{\prime\prime}\text{Q})$ state, which proceeds through the DP trajectory.

3. CONCLUSIONS

Our study suggests the following generalizations: The ESD of A_- ions from physisorbed homonuclear diatomic molecules, A_2^- , are often produced by DA via a transient A_-A_2^- state. The trajectory (DP or IB) of the desorbing A_- ions is uniquely determined by the potential curve of this A_-A_2^- state. Furthermore, the A desorption via the IB trajectory is often quenched or severely reduced except on rare-gas substrates. In contrast, the A desorption via the DP trajectory proceeds, on most surfaces, similarly to A dissociation from gaseous A_2^- .

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